

Preliminary communication

SYNTHESIS AND CHARACTERIZATION OF THE ANION TETRA- μ -HYDRIDOIODOPENTADECACARBONYL TETRARHENATE(1-)

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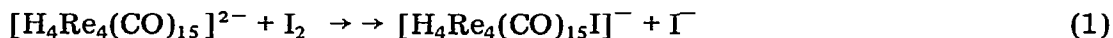
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Summary

The reaction of $[\text{H}_4\text{Re}_4(\text{CO})_{15}]^{2-}$ with ethanolic I_2 gives the novel species $[\text{H}_4\text{Re}_4(\text{CO})_{15}\text{I}]^-$, characterized by IR, NMR and X-ray analysis. The mono-anion contains an open tetrametal array as in the parent species, with the iodide ligand terminally bound to the apical metal atom. The hydridic hydrogen atoms are bridging on the four Re—Re bonds.

The reactions of the anion $[\text{H}_4\text{Re}_4(\text{CO})_{15}]^{2-}$ [1,2] are presently under investigation. We have already reported on its decomposition in boiling ethanol, which gives species such as $[\text{H}_3\text{Re}_3(\text{CO})_{10}]^{2-}$ [3,4], $[\text{H}_3\text{Re}_3\text{O}(\text{CO})_9]^{2-}$ [3,4] and $[\text{H}_4\text{Re}_4(\text{CO})_{13}]^{2-}$ [4,5], and we now report on its reaction with ethanolic I_2 . The salt $(\text{NEt}_4)_2[\text{H}_4\text{Re}_4(\text{CO})_{15}]$ was suspended in ethanol and ethanolic I_2 was added dropwise with stirring at room temperature (molar ratio of the reagents 1/1); a white precipitate slowly separated and was shown to be the new species $(\text{NEt}_4)[\text{H}_4\text{Re}_4(\text{CO})_{15}\text{I}]$. The reaction does not lead, as expected, to fragmentation of the metal atom cluster or to replacement of hydridic hydrogen atoms by iodide ligands but follows the simple reaction 1. This implies that ligand insertion can be described as an electrophilic attack of the I^+ ligand on the parent cluster anion.



The IR spectrum of the new anion in acetone solution shows the following bands due to terminal CO groups: 2085w, 2025s, 1980vs, 1960m, 1935m, 1905m and 1870 cm^{-1} . The NMR spectrum, in CD_3COCD_3 , in the high field region (see Fig. 1) exhibits three signals at τ 25.17 ppm (triplet), τ 25.52 ppm (doublet) ($J(\text{H}-\text{H})$ ca. 3 Hz) and τ 27.36 ppm (singlet) (integration ratios 1/2/1), whose integration with respect to the cationic methylene hydrogens is in good agreement with the proposed stoichiometry.

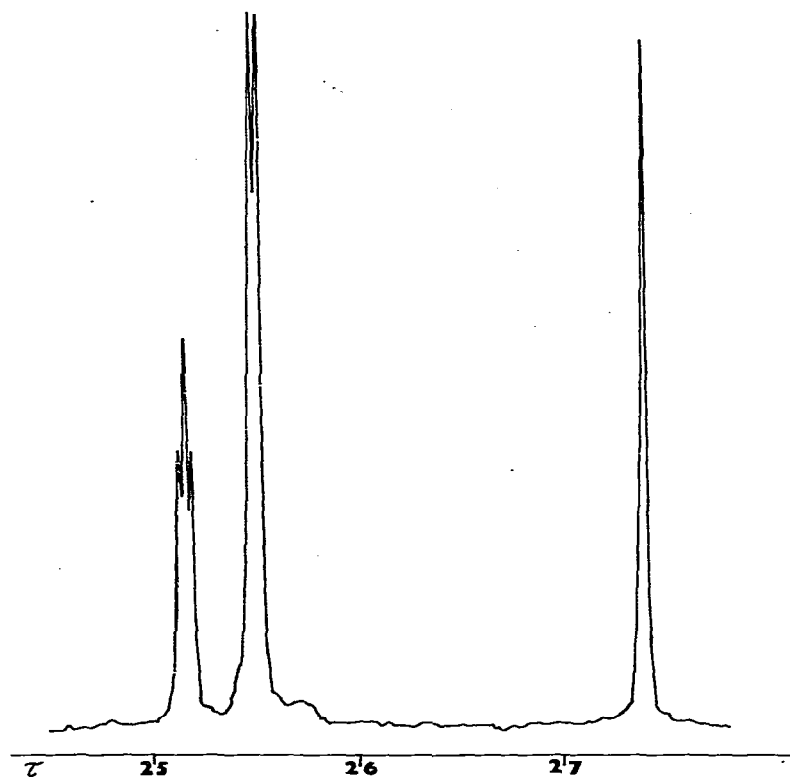


Fig. 1. ^1H NMR spectrum in the hydric region of the anion $[\text{H}_4\text{Re}_4(\text{CO})_{15}\text{I}]^-$ performed in CD_3COCD_3 solution at room temperature.

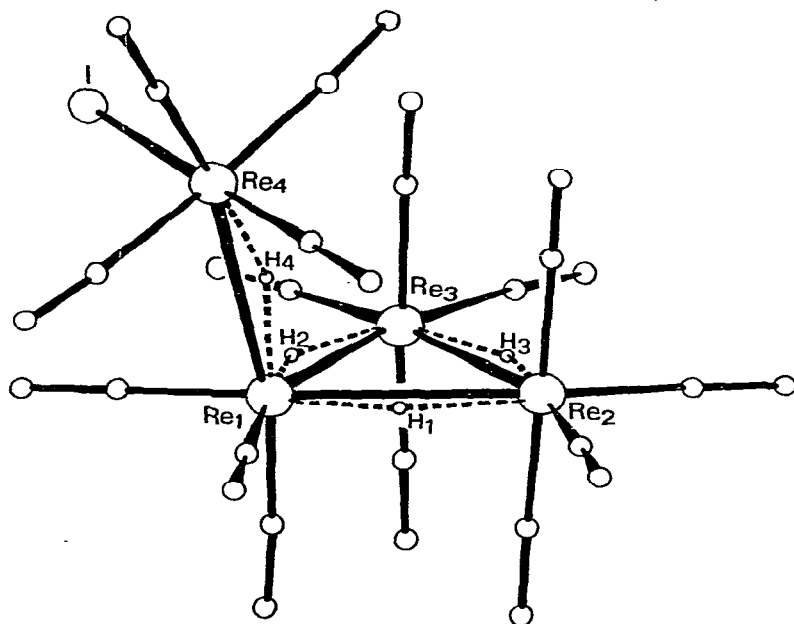


Fig. 2. A view of the anion $[\text{H}_4\text{Re}_4(\text{CO})_{15}\text{I}]^-$ with the postulated hydric atoms positions. The Re—Re bonds are as follows: 1—2 3.249(1), 1—3 3.248(1), 1—4 3.348(1) and 2—3 3.284(1) Å.

The salt has been investigated by X-ray diffraction. It gives colourless triclinic crystals, space group $P\bar{1}$ (No. 2), with a 17.573(5), b 12.552(3), c 8.413(2) Å, α 95.42(3)°, β 86.70(3)°, γ 98.84(3)°, D_m 2.58(2), D_c 2.60 g cm⁻³ for $Z = 2$; $\mu(\text{Mo-K}\alpha)$ 149.2 cm⁻¹. The structure was solved by conventional Patterson and Fourier methods and refined by block-matrix least-squares, on the basis of 3415 significant reflections, up to $R = 0.044$.

The anion $[\text{H}_4\text{Re}_4(\text{CO})_{15}\text{I}]^-$ is shown in Fig. 2. It contains an open tetrametal array very similar to that present in the parent anion. The iodine atom is bound terminally to the apical Re(4) atom (Re(4)—I 2.813(2) Å). The carbonyl ligands are all terminally linked to the rhenium atoms, three to Re(1) and four to each of the other ones (mean Re—C and C—O 1.91 and 1.17 Å). The hydridic hydrogen atoms are bridging on the four Re—Re bonds, as indicated by the values of the metal—metal distances (3.25–3.35 Å) and by the arrangement of the carbonyl ligands. The main differences with respect to the parent anion are as follows: (i) in the apical moiety containing Re(4) the iodide ligand lies in the direction which was occupied by a CO group, while a carbonyl group occupies now the coordination site of the terminally bound hydridic ligand, (ii) this fourth hydridic ligand has migrated to the Re(2)—Re(3) edge which shows a marked lengthening (3.28 vs. 3.03 Å) and (iii) also the remaining metal—metal bonds show a certain lengthening (0.04–0.07 Å) because of the increased steric hindrance of the apical moiety and the consequent higher non-bonding repulsions.

The high field NMR spectrum (Fig. 1) can be interpreted as follows: the signal at τ 25.52 ppm (doublet) of double intensity must be due to the chemically equivalent hydrogen atoms H(1) and H(2). The singlet at τ 27.36 ppm can be assigned to H(3) and the signal at τ 25.17 ppm (triplet) to H(4). This choice is suggested by the fact that coupling is more probable for H(4) which, in its proposed location, is closer than H(3) to H(1) and H(2). Coupling between hydridic hydrogens in NMR spectra of cluster compounds is rather unusual; a coupling ($J(\text{H—H})$ ca. 4 Hz) was observed between a terminal and a bridging hydride in $\text{H}_2\text{Os}_3(\text{CO})_{11}$ [6] but, to our knowledge, this is the first case of coupling between different edge-bridging hydrides. In the parent anion $[\text{H}_4\text{Re}_4(\text{CO})_{15}]^{2-}$ three hydrides were present in positions corresponding to those of H(1), H(2) and H(4) but coupling was not observed, probably because it was obscured by the tautomerism between H(4) and the hydride terminally bound to Re(4) [7].

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